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The results of the hydrogenation of various coals in the liquid phase in an autoclave are given in Table 2. Used as solvents for this series of experiments were: (a) a hydrogenated product boiling above 300° C, (b) residue of the primary tar of coals from the Leninsk occurrence and boiling above 300° C. The data listed show that the yield of liquid products fluctuates between 72 and 91% and depends on the composition of the coal, its properties, and its C/H ratio. Thus, in the hydrogenation of brown coals the yield of liquid products is somewhat lower than that obtained in the hydrogenation of mineral coals and sapropelites.

The yield of solid residue is low and fluctuates between 2.5 and 8.9%. More reaction water is obtained in the hydrogenation of those coals which contain a higher quantity of oxygen (brown coals).

From the data obtained one may draw the following conclusion: the coals which are most suitable for hydrogenation are those in which C/H lies between 8 and 16 and the content of volatile substances in the combustible mass is no lower than 35-36%.

A study of the behavior of various fossil combustibles submitted to hydrogenation shows that the yield of liquid products depends on the composition of the organic substance of the product undergoing hydrogenation. In view of the fact that the final product of hydrogenation is gasoline, which is composed exclusively of hydrocarbons, i.e., substances which contain only carbon and hydrogen, it is expedient to express this relationship by a curve in which the yield of liquid products in percent is plotted against the percentage content of hydrogen referred to carbon, i.e., 100 H/C (cf. Figure 1).

It follows from Figure 1 that

1. All coals for which 100 H/C is no lower than 6.5 are perfectly suitable for hydrogenation. The yield of liquid products from these coals comprises 77-90%.

2. All fossil combustibles can be divided into five basic groups:

Group I, 100 H/C > 12 — petroleum;

Group II, 100 H/C = 9 ÷ 12 — bogheads, liptobiolites;

Group III, 100 H/C = 6.5 ÷ 9.0 — mineral and brown coals;

Group IV, 100 H/C = 5.4 ÷ 6.5 — mineral coals;

Group V, 100 H/C < 5.4 — mineral coals (lean PS).

Only representatives of groups I, II, and III are suitable for hydrogenation.

3. Assuming that in gasolines 100 H/C ≈ 18, one may calculate the approximate expenditure of hydrogen for the reaction. For group I, this expenditure will be approximately 6.0%; for group II, 6.0 to 9.0%, and for group III, 9.0 to 11.5%.

The coals considered above, judging from the results of the hydrogenation, are well suited for this process. Data on the chemical composition of a coal permit, in the first approximation, determination of whether this coal is suitable for hydrogenation. However, a petrographic examination is also necessary before a definite conclusion can be drawn, because the petrographic composition has an influence on the process of hydrogenation. Clarain and durain are liquefied with facility, while fusain, which is highly carbonized, cannot be easily liquefied even at a pressure of 200 atm. (See Table 3.)

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Hydrogenation under pressure of the high-molecular substances of which the crude material is composed begins at 320-300° C, but proceeds effectively only at a temperature of 380-400° C. Above this temperature the dissolved substance of coal undergoes hydrogenation under cracking, which brings about lowering of the specific weight of the total liquid product, a decrease of the asphaltene content, and an increase of the yield of products boiling below 300° C. As an example, the data on hydrogenation of coal from the Main Station of the Cheremkhovo deposit are cited in Table 4. These data show that in the range 420-440° C the yield of liquid hydrogenated products diminishes (consequently there is a higher yield of gas) while the content of light fractions grows and the content of asphaltenes decreases. In the hydrogenated products, as the data of Table 5 show, the content of hydrogen increases. The ration C/H drops from 11.4 for the starting material to 9.6 for the hydrogenated product obtained at 440° C.

As can be seen from Table 5, sulfur is eliminated below 370° C, while oxygen and nitrogen are eliminated on further increasing the temperature.

A still further increase in the temperature of coal hydrogenation will bring about an intensification of fission reactions, leading to the formation of gas and of products of condensation and polymerization. The formation of the latter will result in an increase of the yield of solid residue, an increase which is actually observed already at 460° C. Consequently, it is necessary to carry out the hydrogenation in several stages. In the first stage, which is customarily referred to as liquid-phase hydrogenation, solution of the coal and hydrogenation of the solution take place. The process is conducted at 460-480° C under a hydrogen pressure of 200 to 700 atmospheres. The principal products of this stage of hydrogenation are a broad fraction boiling within the range 300-320° C and consisting of gasoline and medium oil, and a residue boiling above 300-320° C. Besides, the following products result: (a) gas containing CO₂, CO, H₂S, paraffinic hydro-carbons (principally methane, ethane, propane, and butane), and a small quantity of unsaturated hydrocarbons; (b) a solid residue consisting of unreacted coal, the inorganic constituents of coal, and the catalyst; (c) water formed in the reaction.

In the second stage, commonly referred to as vapor-phase hydrogenation, conversion of the medium oil into gasoline takes place. This conversion is carried out over special catalysts in the temperature range 380-520° C under a hydrogen pressure of 200 to 700 atm. The end products are methane, ethane, propane, butane, and higher hydrocarbons. Only small quantities of carbon dioxide and carbon monoxide are formed.

Both in the liquid- and gas-phase hydrogenation, the process is carried out under recyclization of the unconverted oil, to avoid excessive formation of gas.

In the hydrogenation of high-molecular liquid products (tars, mazut, and crude petroleum) as well, the process can not be carried out in one stage, because excessive formation of gas and polymerization and condensation reactions resulting in the formation of undesirable by-products would occur. Under these conditions, the yield of light, colorless products would drop and the yield of gas increase. The polymerized products deposited on the catalyst would interfere with the smooth operation of a continuous process. This is actually confirmed by the experimental results of A. N. Sakhanov and M. D. Tilicheyev (4), who carried out liquid-phase hydrogenations in one stage.

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If, in a single-stage hydrogenation of petroleum residues in an autoclave the yield of gasoline is brought up to 40%, there is a 7.5% loss of gasoline due to conversion into gas. With a 50% yield, this loss is increased to approximately 18%. The hydrogenation of liquid high-molecular substances must also be carried out in two stages, i.e., a broad fraction serving as crude material for the second stage of the process must be obtained in the liquid-phase hydrogenation (first stage of the process) and converted further. The main quantity of gasoline is then obtained in the vapor-phase conversion (i.e., the second stage). Just as in the hydrogenation of coal, the unreacted oil is recirculated.

In the course of the industrial application of the hydrogenation process, it was established that the broad fraction obtained in the first stage (that of liquid-phase hydrogenation) is insufficiently hydrogenated to be processed in the second stage. It still contains a considerable quantity of unsaturated compounds and of nitrogen and oxygen compounds, i.e., substances which shorten the useful life of the vapor-phase catalyst. Research done by M.S. Nemtsov demonstrated the necessity of introducing an intermediate stage, during which the broad fraction forming the product of the first stage of the process undergoes a preliminary hydrogenation prior to the final cracking stage. The intermediate hydrogenation is carried out with the aid of a sulfide catalyst.

The flow sheet of a hydrogenation plant includes units for the production of hydrogen and for the purification of gaseous hydrogenated products from CO_2 , H_2S , and NH_3 -- also equipment for the separation of products into C_5 , C_4 , C_3 , C_2 , and C_1 fractions. The technological schemes of the hydrogenation of liquid crude material and solid crude materials differ from each other only as far as the liquid phase (first stage) is concerned: there is no difference in the second stage (vapor phase). The differences in the first stage are due to the fact that it is necessary to have equipment for the preparation of pastes and the treatment of sludges in the case of coal.

Generally speaking, the flow sheet of a hydrogenation plant consists of the following divisions:

1. Production of hydrogen and its purification;
2. Preparation of the crude material;
3. Liquid-phase hydrogenation;
4. Treatment of sludge;
5. Intermediate hydrogenation;
6. Cracking of the hydrogenated crude material [vapor-phase hydrogenation];
7. Distillation of the products of the three hydrogenation stages;
8. Compressor and pump installations;
9. Separation of gases and their treatment;
10. Aromatization of gasoline

[A flow sheet illustrating the hydrogenation of coal not reproduced here, shows the following equipment units: (1) hydrogen compressor, (2) heat exchanger, (3) high-pressure pipe still, (4) reaction column, (5) hot separator, (6) cooler, (7) gas separator, (8) scrubber for washing the gas with oil, (9) circulation pump, (10) pump for feeding crude material, (11) coal bin, (12) coal-crushing mill, (13) centrifuge, (14) furnace for semicoking (15) pipe still, (16) distillation column, (17) storage tank for medium oil from the liquid-phase hydrogenation stage, (18) storage tank for medium oil from the intermediate hydrogenation, (19) storage tank for gasoline from the intermediate hydrogenation; (20) storage tank for gasoline from the vapor-phase hydrogenation stage, (21) storage tank for oil (to be recirculated) from the vapor-phase hydrogenation stage.

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The units indicated above were used in the following stages:

- I. Liquid phase: 1, 2, 3, 4 (two), 5, 6, 7, 8, 9, 10, 11, 12, 13, 14.
- II. Intermediate hydrogenation: 1, 2, 3, 4 (two), 6, 7, 9, 10.
- III. Vapor phase: 1, 2, 3, 4 (two), 6, 7, 9, 10.
- IV. Distillation of the liquid-phase hydrogenate: 15, 16, 17.
- V. Distillation of the intermediate-stage hydrogenate: 15, 16, 18, 19.
- VI. Distillation of the vapor-phase hydrogenate: 15, 16, 20, 21.

BIBLIOGRAPHY

- 1. M. S. Nemtsov, Symposium "Destructive Hydrogenation of Fuels," Gostoptekhisdat, 1934.
- 2. M. S. Nemtsov, Uspekhi Khimii, No 11, 1653, 1938.
- 3. I. B. Rapoport, Zhurnal Fizicheskoy Khimii, 9-10, 1940.
- 4. A. N. Sakhanov and M. D. Tilicheyev, Work of the Conference on Cracking and Hydrogenation, Groznyy, 1931.

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Table 1. Results of the Hydrogenation of Various Types of Donets Coal

Conditions of experiment: temperature 420° C; initial hydrogen pressure 80 atm; ratio of solid to liquid = 1:1; catalyst MoS₃ (1%)

Type of Coal	Elementary Composition (in %)			Results of Hydrogenation (% referred to dry, ash-free paste)				
	C	H	O+N	$\frac{O+N}{H}$	$\frac{C}{H}$	Oil	Water Formed in Reaction	Expenditure of Hydrogen
Gas G	84.53	5.28	10.19	1.93	16.0	82.40	5.58	1.56
Bituminous PZh (parovichnyy zhirnyy)	85.21	5.34	9.45	1.76	16.1	79.28	3.15	1.16
Coking K	87.79	4.78	7.43	1.55	18.3	72.93	3.69	1.09
Lean T	90.43	4.03	5.54	1.37	22.4	52.25	2.79	0.91
Anthracite	97.38	1.69	0.93	0.55	57.5	53.97	0.0	0.84

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Table 2. Results of the Hydrogenation of Various USSR Coals

Conditions of experiment: temperature 400-440° C; initial hydrogen pressure 80-100 atm; duration 90-120 minutes; catalyst MoS₃ (1%); ratio of solid to liquid=1:1

Origin of Coal	Characteristics of Coal (%)				Yield of Hydrogenation Products (% referred to dry ash-free charge)			Expenditure of Hydrogen (% referred to dry, ash-free paste)
	AC (ash content)	C	H	C/H	Liquid Products	Water Formed in Reaction	Solid Residue	
Matagan (boghead)	12.00	76.81	9.67	7.95	84.84	--	--	--
Barzas	28.18	79.91	7.40	10.80	91.63	--	--	2.07
Cheremkhovo - sump stratum	16.35	75.35	5.67	13.25	82.62	5.37	2.43	--
- main stratum	11.72	77.60	5.97	13.00	87.6	5.9	3.70	--
Leninsk								
Zhurinsk stratum	4.76	78.66	6.40	14.60	87.37	--	--	5.90
Meyerovsk "	3.46	80.41	5.96	13.50	87.0	4.12	3.62	--
Baykaimsk "	3.04	80.44	5.87	11.65	86.10	4.05	3.91	6.00
Chelyabinsk	11.74	72.72	5.05	14.40	78.80	7.21	4.68	2.24
Chernovsk								
Kandalinsk region	6.70	73.81	5.15	14.30	89.1	--	5.10	4.4
Leninsk pit No 2	9.06	74.54	5.20	--	83.0	--	--	--
Tormovsk, Naklonnaya pit and Vertikal'naya pit	8.59	74.49	5.26	--	90.5	--	--	--

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Table 2 (contd)

Origin of Coal	Characteristics of Coal (%)				Yield of Hydrogenation Products (% referred to dry ash-free charge)			Expenditure of Hydrogen (% referred to dry, ash-free paste)
	A ^c (ash content)	C ^r	H ^r	C ^r H ^r	Liquid Products	Water Formed in Reaction	Solid Residue	
Minusinsk								
Run-of-the-mine coal	8.33	79.60	5.42	14.70	78.4	--	4.55	4.6*
Pit No 7, Velikan stratum	7.61	79.21	5.74	--	81.5	--	--	--
Pit No 3, Moshchny "	7.62	79.95	5.70	--	80.6	--	--	--
Pit No 7, Dvukharshinny stratum	8.02	79.80	5.66	--	81.5	--	--	--
Artemovsk (blend of coal from shafts 6/6, 2S, and 2/5)	11.57	71.05	5.90	12.10	88.9	6.7	7.8	4.1*
Moscow Basin, grade 0	23.60	70.03	5.32	13.20	77.44	7.54	5.27	4.60
Sangar (run of the mine)	15.61	78.88	5.80	13.60	90.64	--	--	4.18
Raychikhinsk (average dynamic sample)	9.65	70.51	4.41	16.00	72.25	5.55	8.96	--
El'ga	22.75	64.72	5.78	11.20	80.2	--	--	--
Bureinsk:								
Chalanykh stratum	23.5	80.80	5.93	13.65	86.62	--	4.57	--
Verkhnyaya El'ga stratum	33.8	77.43	6.27	12.32	83.80	2.93	4.00	--

* Expenditure of hydrogen referred to combustible substance of coal.

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Table 3. Hydrogenation of Individual Constituents of Coal

Conditions of experiment: temperature 400° C; duration 180 minutes; initial hydrogen pressure 80 atm; catalyst $\text{Sn}(\text{OH})_2$ (1%)

Coal Constituent Used as Crude Material	<u>Characteristics</u> (%)				<u>Results of Hydrogenation,</u> (% referred to dry, ash-free paste)			Content of Combustible Matter (C+H) in Solid Residue (% Re- ferred to combustible substance of coal)
	<u>A^c</u>	<u>C</u>	<u>H</u>	<u>C H</u>	<u>Yield of Liquid Products</u>	<u>Yield of Gas</u>	<u>Expenditure of Hydrogen</u>	
Clarain of coal from the Tkvarcheli deposit, stratum 1-a	9.86	85.70	5.71	15.00	86.45	5.19	3.08	6.33
Vitrain of coal from Tkibuli deposit, Len- insk district	2.81	79.80	5.31	15.02	85.23	4.10	2.67	12.05
Fusain of brown coal from Gusinoe Ozero deposit	7.96	80.93	3.90	20.75	--	5.23	1.79	70.21

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Table 4. Hydrogenation of Coal From the Chermkhovo Deposit at Various Temperatures

Conditions of experiment: initial hydrogen pressure 100 atm; ratio of solid to liquid 1:1, catalyst MoS_3 (1%)

Rate of Heating (°C per min)			Characteristics of Hydrogenation Products							
Up to 340° C	From 340° C to Reaction Temp	Temp of Expt °C	(Yield) (% referred to organic substance)		Sp Gr of Hydro- genate	Content of Ashphal- tenes (%)	Yield of Individual fractions (% referred to combustible substance of charge)			Yield of Hydrogen (%) referred to combustible substance)
			Hydro- genate	Solid Residue			up to 200° C	up to 300° C	above 300° C	
0.9	0.4	360	77.5	15.85	--	40.2	0.65	7.9	69.5	2.8
1.0	0.6	370	82.6	--	--	45.4	0.8	7.6	74.1	2.9
0.9	0.6	380	87.5	9.32	1.104	44.2	1.7	7.3	78.5	3.2
1.6	0.6	390	87.8	6.52	1.086	28.6	2.2	10.3	75.4	--
1.9	0.5	400	91.7	2.98	1.052	31.3	3.4	11.5	76.8	--
1.5	0.5	420	84.5	2.76	1.035	16.8	4.1	15.9	64.6	4.5
1.3	0.5	430	81.5	2.38	--	14.3	5.6	13.6	62.0	4.6
1.1	0.5	440	79.5	2.54	1.022	13.1	--	--	--	4.8
1.1	0.5	460	70.2	3.51	1.001	11.3	12.0	19.8	38.8	5.5

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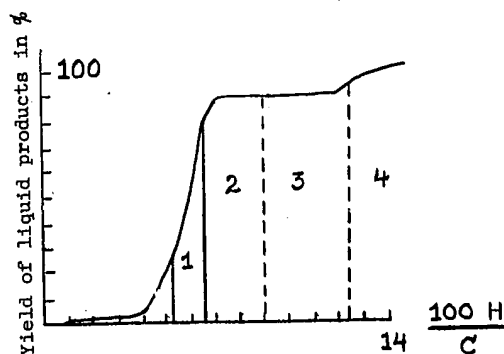
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Table 5. Elementary Composition of Hydrogenate

Crude Material or Product	Composition (in%)				$\frac{C}{H}$
	C	H	S	O + N	
Starting material	80.50	7.08	0.81	11.66	11.4
Hydrogenate from experiment run at 370° C	85.24	8.18	0.08	6.50	10.4
Hydrogenate from experiment run at 410° C	86.38	8.57	0.07	4.98	10.1
Hydrogenate from experiment run at 440° C	87.12	9.04	0.04	4.80	9.6

Figure 1. Dependence of the Yield of Liquid Products on $\frac{100 H}{C}$

1. Coal, $\frac{100H}{C} = 5.4 \div 6.2$, $v^2 < 37\%$
2. Coal and lignite, $\frac{100H}{C} = 6.6 \div 9.0$, $v^2 = 37 \div 0\%$
3. Bogheads and liptobiolites, $\frac{100H}{C} = 9 \div 12.5$, $v^2 = 50.0\%$ and higher
4. Petroleum products, $\frac{100H}{C} > 12.5$.

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